Optimization of Warm-Cloud Seeding Agents by Microencapsulation Techniques [1]

LOREN D. NELSON and BERNARD A. SILVERMAN—*Air Force Cambridge Research Laboratories, Bedford, Mass.*

ABSTRACT—Microencapsulation technology, whereby single crystals or solution droplets are chemically "packaged" inside thin coating shells, provides a method of optimizing the chemical and physical properties of warm-cloud seeding agents. Ethylcellulose-encapsulated urea and sodium chloride particles have been produced in the laboratory and their hygroscopic properties investigated gravimetrically, microscopically in a diffusion chamber, and optically in a large fog chamber.

These investigations indicate that microencapsulation provides for a relatively narrow particle spectrum with a sharp lower size limit, gives the particles more structural integrity, prevents degeneration of the particle spectrum and formation of "fines" during handling and dispersal, and greatly reduces clumping and caking during storage, handling, and dissemination. Hygroscopic properties of the seeding particles are not affected by the presence of the encapsulating coating.

As an encapsulated particle grows by vapor diffusion in a humid environment, its core material is released by diffusion through its permeable but insoluble ethylcellulose shell. Individual seeding particles are thus unmistakably "tagged," providing an objective method for evaluating the seeding effects. The process lends itself to large-scale production and promises to be more economical than mechanical milling and sizing to an equivalent size spectrum.

1. INTRODUCTION

In recent years, an increasing amount of attention has been focused on the modification of warm fog and warm cumulus clouds by hygroscopic particle seeding (see e.g., Biswas et al. 1967, Schock 1968, Kocmond 1969, Silverman 1970). These studies have emphasized that the effectiveness of the hygroscopic treatment is highly dependent on the size and concentration of the seeding particles. The most commonly used hygroscopic seeding agent has been sodium chloride, sized by mechanical milling and sorting and stabilized by the addition of free-flowing agents. Sodium chloride, like most other potentially useful hygroscopic chemicals, is, however, corrosive to metals and detrimental to plant life. Such materials are not practical for use in populated areas or over airport runways. Kunkel and Silverman (1970) investigated the fog clearing capabilities of numerous hygroscopic chemicals and found that urea was most practical since it is noncorrosive to metals, nontoxic, and beneficial to plant life. These findings are supported by those of Cress (1970) and Kocmond et al. (1970). Urea, however, has a soft, friable, crystalline structure that fragments easily during handling, producing large numbers of submicrometer-sized particles. Seeding particles of this size are not capable of either producing a visibility improvement in warm fog (Silverman and Kunkel 1970, Jiusto et al. 1968) or stimulating the rain process in warm convective clouds (Smith et al. 1968).

Microencapsulation technology, whereby particles are packaged inside thin coating shells, has been exploited to provide for the control and maintenance of the seeding particle size spectrum. The effects of microencapsulation on the microphysical and chemical properties and, thus, on the warm-cloud seeding potential of hygroscopic materials, are discussed in this paper. The optimization of urea and sodium chloride, in particular, as warm cloud seeding agents is described.

2. MICROENCAPSULATION TECHNOLOGY

Microencapsulation may be defined as a special technique of chemical packaging whereby very small crystals, particulates, or solution droplets are encased in thin coating shells. Possible encapsulation methods include organic phase separation, aqueous coacervation, meltable dispersion, and interfacial polymerization. Potential wall materials include nearly all waxes, and polymers possessing sharp melting points. By proper choice of capsular wall material, wall thickness, and morphology, microencapsulation can be used to alter significantly the chemical and physical properties of the encapsulated substance. Microencapsulation techniques are widely used in foodstuffs, pharmacology, and chemical engineering. A well-known example is the "tiny time pills" advertised by several commerical cold-remedies that employ microencapsulation to effect a controlled, sustained release of the pharmaceutical contents. A detailed review of microencapsulation techniques, effects, and usages is given by Herbig (1967).

All microencapsulations discussed in this paper use ethylcellulose as the wall material, deposited on urea and sodium chloride particles by the process of organic phase separation. [2] They are intended to serve as examples only. Other wall materials, encapsulation techniques, and hygroscopic seeding agents can be used.

[2] The microencapsulated seeding agents considered in this paper were fabricated under contract by the Capsular Products Division, National Cash Register Co., Dayton, Ohio.
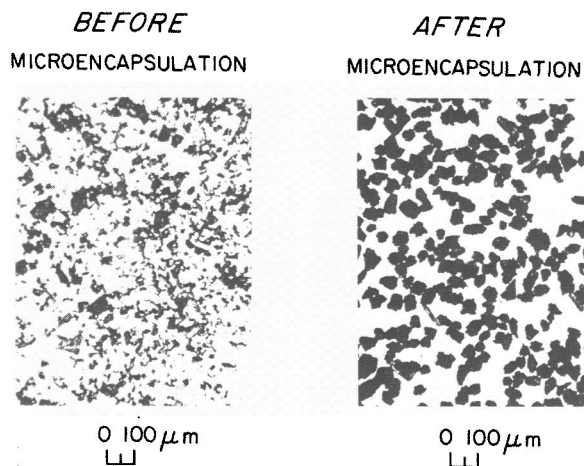
BEFORE
MICROENCAPSULATION

AFTER
MICROENCAPSULATION

0 100 μm

0 100 μm

FIGURE 1.—Photomicrographs of urea particles before and after microencapsulation (batch AP 384).

FIGURE 2.—Cumulative mass distributions of urea particles before and after microencapsulation (batch AP 384).

Liquids as well as dry substances can be encapsulated. The production of micro capsules containing two or more different immiscible hygroscopic crystals is also possible. By using soluble wall materials, it may be possible to achieve delayed and/or controlled release of hygroscopic substances relative to particle resident time within the seeded volume.

3. PROPERTIES OF ENCAPSULATED HYGROSCOPIC PARTICLES

Particle Size Control

Photomicrographs of urea particles before and after microencapsulation are shown in figure 1. One can see that the raw urea sample contains numerous submicrometer particles, the particle size range extending down to the limit of resolution of the microscope. The encapsulated urea sample, on the other hand, indicates that the very small particles have been essentially eliminated. During the encapsulation process, the small fragments adhere to the larger particles to form aggregates of ethylcellulose-coated urea particles. In this sample, the ethylcellulose concentration per particle is approximately 10 percent by mass. An 80-μm diameter particle, for example, has an average shell thickness of about 2 μm. Figure 2 gives the cumulative mass distributions of the urea samples shown in figure 1. The effect of the microencapsulation has been to narrow the size spectrum by eliminating particles less than 20 μm in diameter. Both the size at which this cutoff occurs and the modal size of the distribution can be controlled by varying the encapsulation parameters. Since the encapsulating coating gives the particles structural integrity, further size control by mechanical sorting is also possible if desired.

Kocmond and Eadie (1969) demonstrated that careful sizing of hygroscopic seeding agents significantly improves their fog clearing effectiveness. A dramatic increase in the
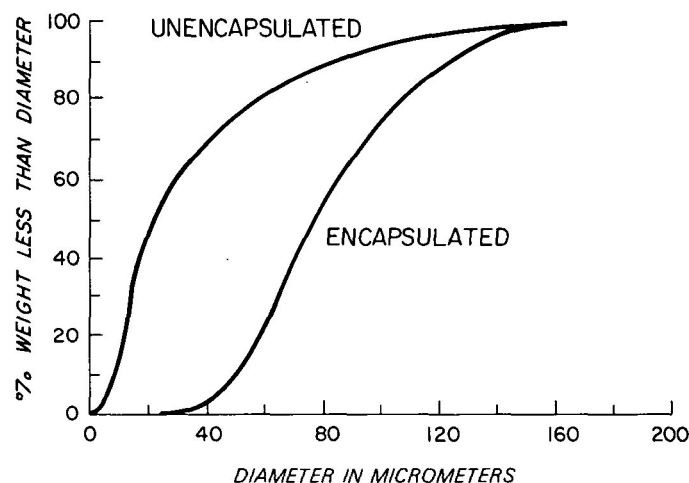
maximum visibility improvement factor produced by sodium chloride seeding in a fog chamber was achieved when the percentage of particles in the desired size range was increased.

The cost of producing encapsulated hygroscopic particles is favorable when compared to the cost of obtaining an equivalent size spectrum by mechanical milling and sorting. In the case of urea, which has a highly fragile crystalline structure, microencapsulation is the only practical means of obtaining particle size control and stability. The production of urea particles that are suitably sized for most warm-cloud seeding operations by mechanical milling and sorting would be prohibitively expensive if not impossible. The pilot-scale cost of producing microencapsulated urea is approximately $1.85 per pound. Large-scale production costs are estimated to be $0.35 to $0.50 per pound.

Particle Size Stability

Hygroscopic seeding agents tend to absorb water vapor prematurely and clump during storage, handling, and dissemination. Kocmond and Eadie (1969) found that a substantial amount of clumping occurred in the aircraft hoppers during their fog dispersal tests, reducing the efficacy of their carefully presized sodium chloride seeding particles. A significant reduction in clumping as well as in fragmentation is achieved by microencapsulation. Figure 3 shows unencapsulated and encapsulated samples of urea after exposure to identical environmental conditions; that is, bulk samples of each were exposed for 2 hr in air having a relative humidity of 90 percent. Note that the raw material has been transformed into hard lumps up to ¼ in. in diameter. The encapsulated material, on the other hand, has retained its original free-flowing powder consistency, its size spectrum being almost completely unchanged. The relative condition of encapsulated and unencapsulated sodium chloride particles after storage for
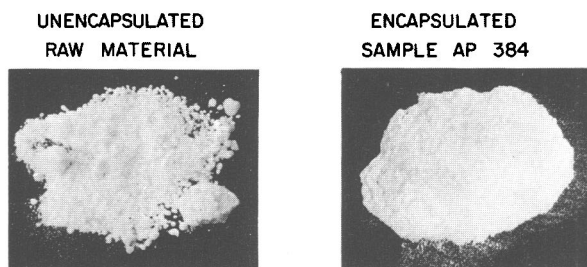
FIGURE 3.—Photographs of unencapsulated and microencapsulted urea (batch AP 384) after exposure in bulk to a humid environment at 90 percent relative humidity for 2 hr.
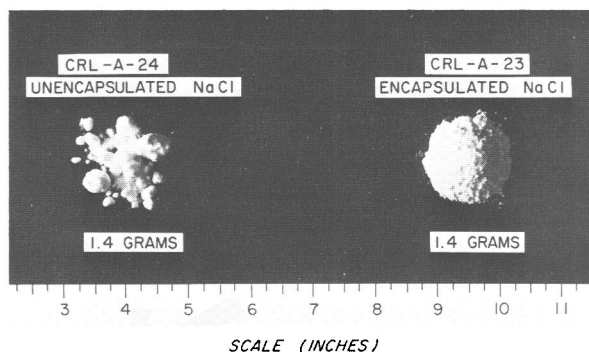

FIGURE 4.—Photographs of unencapsulated and microencapsulated sodium chloride after 9 mo storage in identical closed glass containers.
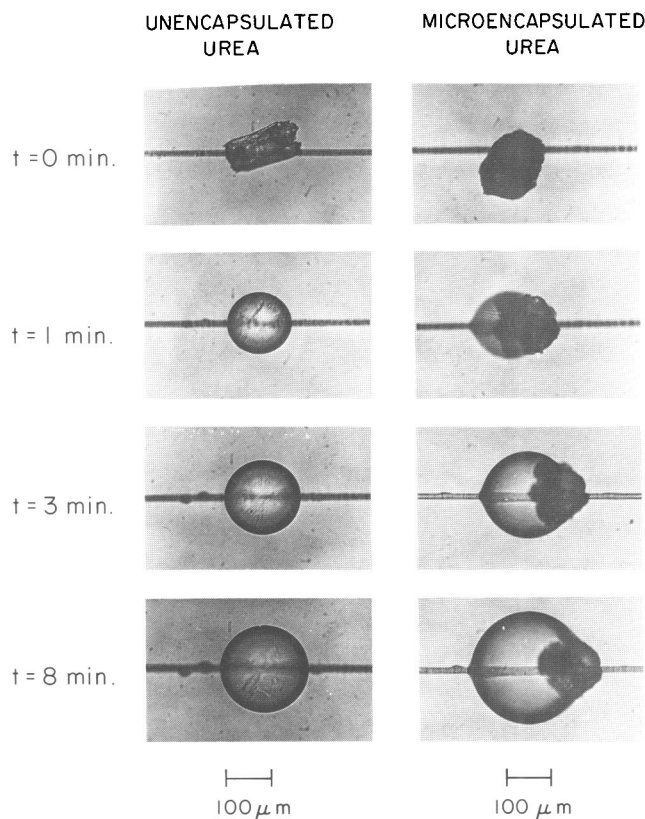

FIGURE 5.—Comparative photomicrographs of an individual unencapsulated urea particle and a microencapsulated urea particle at several stages in their growth. The particles are suspended from 10-μm glass fibers in a chamber maintained at 100 percent relative humidity and are taking on water with time. The initial sizes of the unencapsulated and encapsulated urea particles are not equal.

9 mo in identical closed glass containers is shown in figure 4, indicating that stability of the size spectrum during storage is also improved by microencapsulation. It should be pointed out that bulk water uptake is not reduced by the microencapsulation. Clumping is significantly reduced, presumably as a result of the elimination of the direct surface-to-surface contact between the partially wetted hygroscopic particles.

Hygroscopicity

The ethylcellulose encapsulating wall is insoluble in, but permeable to, water vapor, water, and urea solution. As an encapsulated particle grows by condensation in a humid environment, its core material is released by diffusion through the ethylcellulose shell. Initial water uptake occurs at a preferred site(s) on the nonspherical particle, this site(s) being the center for the further growth of the particle. Thus, the particle remains irregular in shape as it grows by condensation. An unencapsulated urea particle, on the other hand, becomes spherical after it dissolves and remains sperical as it grows. The typical appearances of encapsulated and unencapsulated urea particles at various stages of their growth, which illustrate this feature, are shown in figure 5.

The hygroscopic properties of encapsulated and unencapsulated particles have been investigated by observing their rates of growth in a controlled temperature-humidity
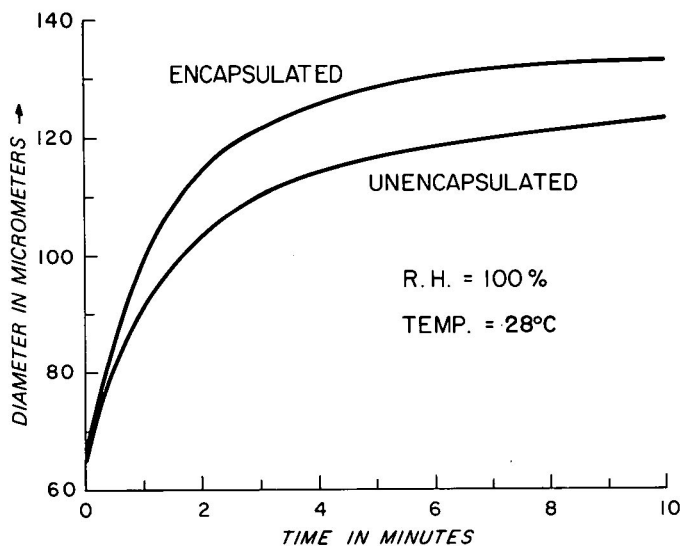

FIGURE 6.—Comparison between the experimental growth rates of an unencapsulated and a microencapsulated urea particle (batch AP 384) as they take on water at 100 percent relative humidity. The growth rates were measured microscopically in a controlled humidity chamber.
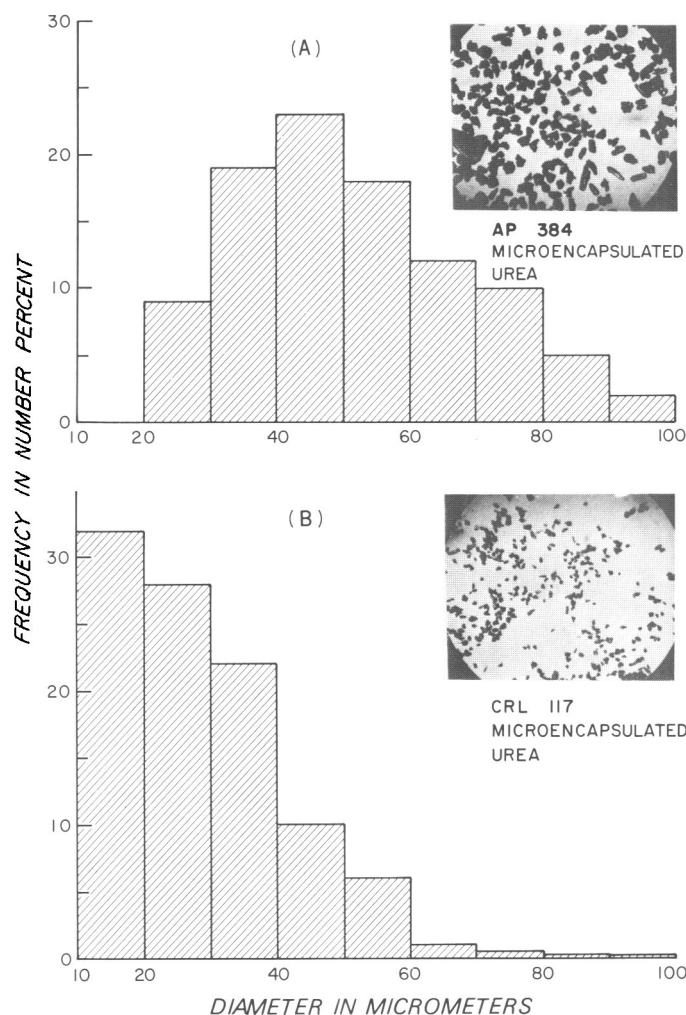
FIGURE 7.—Size distributions of microencapsulated urea (A) batch AP 384 and (B) batch CRL 117.

environment. The sizes attained by 65-μm initial diameter encapsulated and unencapsulated urea particles as they grow in a 100-percent relative humidity environment at 28°C are shown as a function of time in figure 6. In view of the uncertainty in determining the size and urea content of the irregularly shaped encapsulated particle as it grows, it can only be concluded that ethylcellulose encapsulation has no significant effect on the hygroscopic properties of urea.

Identification of Seeding Effects

Because the ethylcellulose coating on each particle is insoluble in water, both the droplets formed on the seeding nuclei and the natural cloud droplets are readily distinguishable. A seeding agent having a signature such as this should be invaluable in the evaluation of warm-cloud seeding experiments. By analyzing cloud droplet samples for the presence of the ethylcellulose shells, the effectiveness and areal extent of the seeding can be determined. The encapsulated particles can also be used in controlled

experiments to obtain an objective record of the effects of coalescence.

4. SEEDING EFFECTIVENESS

Tests of the seeding effectiveness of microencapsulated urea were carried out in the large 30-ft diameter fog chamber at the Cornell Aeronautical Laboratory, Buffalo, N.Y. As discussed by Kocmond et al. (1970), reproducible fogs can be created and maintained inside the chamber. Jiusto et al. (1968) investigated the physical characteristics of fogs produced within the chamber and found them to be very similar to typical inland radiation fog in terms of droplet radius, droplet radius range, liquid water content, droplet concentration, and visibility.

Two size distributions of microencapsulated urea, identified as AP 384 and CRL 117 in figure 7, were tested in the fog chamber. It can be seen in figure 7 that the AP 384 microencapsulated urea is characterized by a size spectrum having a modal diameter of 45 μm, having approximately 90 percent of its particles by number between 20 and 80 μm in diameter, and having virtually no particles less than 20 μm in diameter. The CRL 117 microencapsulated urea has a modal diameter of 15 μm, has approximately 90 percent of its particles by number between 10 and 60 μm in diameter, and has almost no particles less than 10 μm in diameter. In accordance with the computational results of Jiusto (1968) and Silverman and Kunkel (1970) that showed that the use of larger seeding particles requires larger seeding rates, the laboratory fog was seeded with 210 and 25 gm of AP 384 and CRL 117 microencapsulated urea, respectively.

The results of the AP 384 microencapsulated urea seeding experiment are shown in figure 8. One can see that significant improvements in visibility were achieved in the chamber due to seeding. At the upper level, 15 ft above the chamber floor, the visibility improved from an initial value of 400 ft to a value of 13,600 ft within 4 min after seeding. Typical runway visual range (RVR) minimums of ¼ mi were exceeded within 3 min. At the lower level, 4 ft above the chamber floor, the initial visibility of 200 ft improved to 6,700 ft, RVR minimums being achieved approximately 9 min after seeding. The result of a model calculation in which the fog and seeding parameters are similar to those in the fog chamber test is also shown in figure 8. The model calculation does, however, include the effects of turbulent diffusion that, it can be seen, limit both the maximum visibility improvement and the duration of the clearing.

Table 1 presents the results of the AP 384 and CRL 117 microencapsulated urea tests together with those obtained by Kocmond and Eadie (1969) in fog chamber tests of several other hygroscopic materials. The generally higher visibility improvement factors produced by the microencapsulated urea seeding are attributed primarily to the excellent size control attained through microencapsulation.
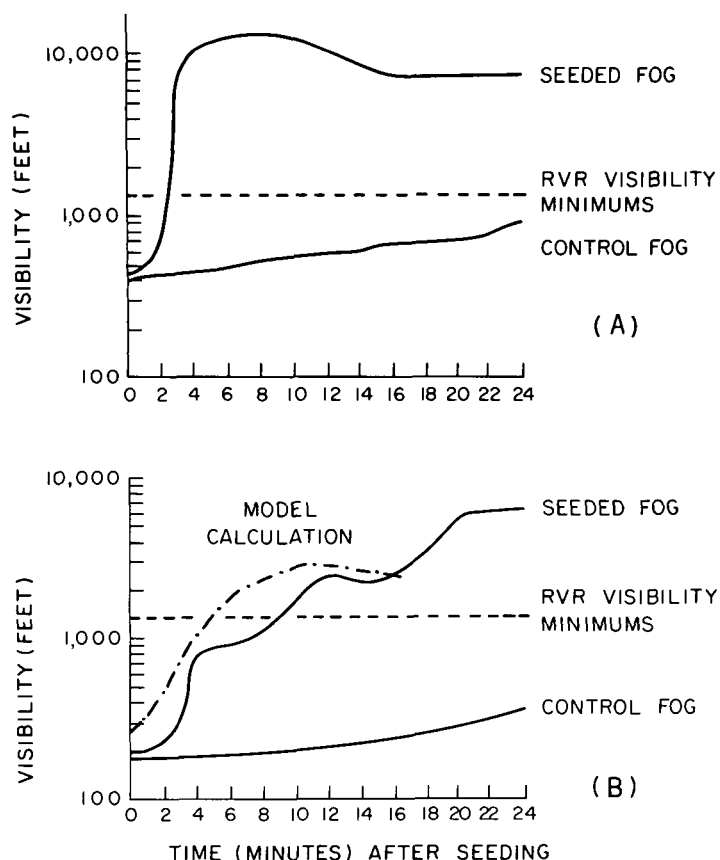
FIGURE 8.—Visibility improvement attained in chamber seeding tests with microencapsulated urea, batch AP 384, at a seeding rate of 0.35 g·m⁻³: (A) 15 ft above chamber floor and (B) 4 ft above chamber floor.

5. CONCLUSIONS

Microencapsulation technology is a practical means of optimizing the effectiveness of warm-cloud seeding agents. Properties and effects which have been made possible by the encapsulation of urea and sodium chloride particles with ethylcellulose include:

1. Control of the particle size distribution.

2. Improved structural integrity permitting further size selection by mechanical means if desired.

3. Establishment of a sharp lower limit to the particle size spectrum.

4. Improved flowability of the seeding particles.

5. Improved physical and chemical stability of the seeding particles during storage, handling, and dissemination.

6. Objective identification and evaluation of the areal extent of seeding, seeding effectiveness, and coalescence efficiency by analyzing cloud and precipitation particles for the presence of insoluble capsular wall material.

TABLE 1.—*Visibility improvement factors* for some seeding agents tested in the 600 m³ cloud chamber*

Seeding mass (gm)	Seeding agent	Particle distribution		Max. visibility improvement factor (4-ft level)
		Mode (μm)	Size range (μm)	
5	NaCl	4	90% 1–9	7. 5
5	NaCl	8	85% 1–11	6. 2
5	NaCl		95% 5–20	24. 0
10	NaCl	8	85% 1–11	13. 2
125	NaCl		44–125	6. 1
5	NaCl		4–20	6. 6
6	NH₄NO₃-Urea-Water	4	2–20	1. 5
15	NH₄NO₃-Urea-Water	4	2–20	4. 7
30	NH₄NO₃-Urea-Water	4	2–20	6. 1
5	Calcium Chloride			5. 8
5	Sodium Nitrate		5–40	2. 0
5	Disodium Phosphate		95% 4–20	7. 1
210	AP 384 Microencapsulated Urea	45	90% 20–80	16. 6
25	CRL 117 Microencapsulated Urea	15	90% 10–60	9. 7

*Visibility improvement factor is defined as the ratio of the visibility of the seeded fog to the visibility of the control fog at the same time after initiation of the expansion.

REFERENCES

Biswas, K. R., Kapoor, R. K., Kanuga, K. K., and Ramana Murty, Bh. V., "Cloud Seeding Experiment Using Common Salt," *Journal of Applied Meteorology,* Vol. 6, No. 5, Oct. **1967,** pp. 914–923.

Cress, Ted S., "Factors in Warm Fog Dissipation," M.S. thesis, Colorado State University, Fort Collins, Mar. **1970,** 125 pp.

Herbig, James A., "Microencapsulation," *Encyclopedia of Chemical Technology,* 2d Edition, Vol. 13, John Wiley & Sons, Inc., New York, N.Y., **1967,** pp. 436–456.

Jiusto, James E., Pilié, Roland J., and Kocmond, Warren C., "Fog Modification With Giant Hygroscopic Nuclei," *Journal of Applied Meteorology,* Vol. 7, No. 5, Oct. **1968,** pp. 860–869.

Kocmond, Warren C., "Dissipation of Natural Fog in the Atmosphere," *NASA Special Publication* No. SP–212, National Aeronautics and Space Administration, Washington, D.C., **1969,** pp. 57–74.

Kocmond, Warren C., and Eadie, William J., "Investigation of Warm Fog Properties and Fog Modification Concepts," *Cornell Aeronautical Laboratory Technical Report* No. RM–1788–P–22, Buffalo, N.Y., Dec. 31, **1969,** 61 pp.

Kocmond, Warren C., Pilié, Roland J., Eadie, William J., Mack, Eugene J., and Leonard, Richard P., "Project Fog Drops, Investigation of Warm Fog Properties and Fog Modification Concepts," *Cornell Aeronautical Laboratory Technical Report* No. RM–2864–P–1, Buffalo, N.Y., Sept. 1, **1970,** 102 pp.

Kunkel, Bruce A., and Silverman, Bernard A., "A Comparison of the Warm Fog Clearing Capabilities of Some Hygroscopic Materials," *Journal of Applied Meteorology,* Vol. 9, No. 4, Aug. **1970,** pp. 634–638.

Schock, Martin R., "Analysis of a Randomized Salt Seeding Experiment on Cumulus Clouds," *Progress Report* No. 68–8, Contract No. 14–06–D–5979, Institute of Atmospheric Sciences, South Dakota School of Mines and Technology, Rapid City, Aug. **1968,** 40 pp.

Silverman, Bernard A., "An Appraisal of Warm Fog Modification," *Bulletin of the American Meteorological Society,* Vol. 51, No. 5, May **1970,** p. 420.

Silverman, Bernard A., and Kunkel, Bruce A., "A Numerical Model of Warm Fog Dissipation by Hygroscopic Particle Seeding," *Journal of Applied Meteorology,* Vol. 9, No. 4, Aug. **1970,** pp. 627–633.

Smith, Theodore B., MacCready, Paul B., Jr., and Hozaki, Shigemi, "Analysis of Warm Cloud Modification Potential," *Final Report, Part B, Project Skywater,* Contract No. 14–06–D–6447, Meteorology Research, Inc., Altadena, Calif., June 30, **1968,** 68 pp.